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The acquisition of the custom-designed Nanonics Multiview 400 Combined microRaman, Scanning Probe Microscope (SPM), and Nanoindenter system equipment will allow us to bridge the divide between the fundamentals of materials science, chemistry, physics, biology, nanomanufacturing, and engineering, and it serves as a unique training platform for students from science and engineering. Such combined system integration permits correlation of SPM topography of a sample surface with microRaman spectra, and it enables the characterization of local mechanical, chemical and electrical properties in-situ and simultaneously in active polymers and nanocomposites.
Due to the custom-built nature of the equipment and the fact that receipt of the DURIP funds were delayed, the equipment was finally delivered on January 2009. Installation took place within a month, and was completed by end of February 2009. Two researchers in PI Ounaies' group were trained on most of the functions. So far, the focus has been on getting familiar with the SPM, nanoindentation and Raman spectroscopy functions. In the next few months, the focus will shift to the unique features such as the combined Raman and nanoindentation and the SPM/Raman combination.

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ACQUISITION OF A COMBINED MECHANO-ELECTRO-CHEMICAL CHARACTERIZATION EQUIPMENT FOR ADVANCED NANOCOMPOSITES RESEARCH AND EDUCATION

Defense University Research Instrumentation Program 2007

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ABSTRACT

We have acquired a custom-designed Nanonics Multiview 400 Combined microRaman, Scanning Probe Microscope (SPM), and Nanoindenter system. Such combined system integration permits correlation of SPM topography of a sample surface with microRaman spectra. The Nanonics SPM/NSOM component generates surface morphology images while Raman components can measure electrical properties and chemical signatures. The presence of the Nanoindenter allows simultaneous detection of Raman peaks under stress. The broad goal is to permit characterization of local mechanical, chemical and electrical properties *in-situ and simultaneously* in active polymers and nanocomposites. The proposed equipment will greatly impact an ongoing AFOSR project on active nanocomposites, as well as ongoing and proposed DoD and NSF projects lead by the PIs. The capabilities of the custom-designed Nanonics expand to nanoscale mechanical, electrical, and chemical properties of metallic and ceramic thin films and coatings, and MEMS and NEMS devices, extending its impact to a variety of ongoing and future collaborations and research projects. The combination of micron-scale and nano-scale techniques in the proposed equipment makes it uniquely capable of bridging the gap between interfacial interactions and macroscale properties in advanced materials in general and nanostructured materials in particular. The surface morphological information, internal stress, and electrical properties of such materials have been studied separately and the structure-property is yet to be related intrinsically. Having such a system will enable us to investigate the interfacial forces between components and understand the effects of molecular structure and inclusion distribution on nanocomposites. The simultaneous capabilities of the custom-designed equipment are unique and will complement and expand our research and current materials characterization infrastructure, specifically in the area of multifunctional materials.

Due to the custom-built nature of the equipment and the fact that receipt of the DURIP funds were delayed, the equipment was finally shipped to our laboratory in January 2009. The complexity of the equipment required that an engineer from Nanonics travels to our laboratory to install it and train users. By end of February, the equipment was operational and two researchers were trained on most of its functions. The following months, the focus was on testing and getting familiar with each of the three operations: The Scanning probe microscope, the nanoindentation, and the Raman spectroscopy. In the next step, presently and for the next month, the researchers are training on using the unique features such as the combined Raman and nanoindentation, and SPM and Raman.

1.Description of the Acquired Equipment.

Figure 1 shows the equipment in our laboratory. We were given a new space in the basement of our main building to accommodate the equipment and ensure that no ambient vibrations will disturb its operation.

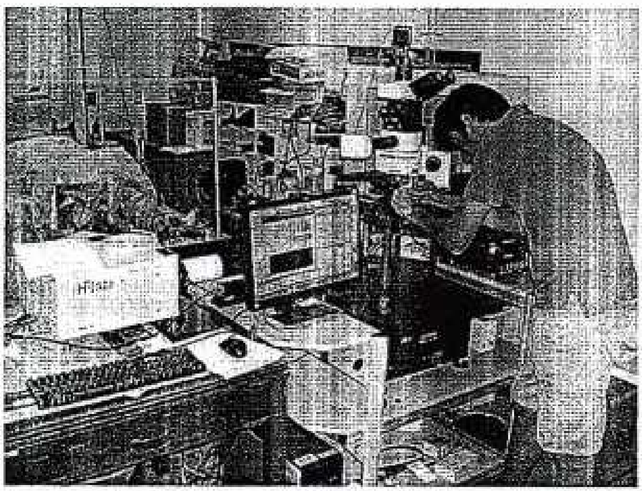
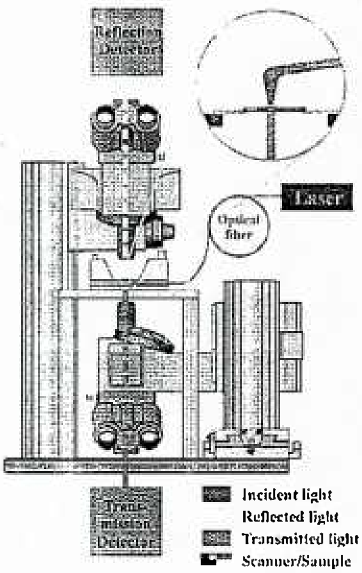


Figure 1. Installed equipment.

The basic idea of this system is to combine the nanoindentation and nanoscratch with scanning imaging analysis. The SPM images and measures surfaces on a nanometer length scale within a few layers of atoms. With a sharp tip, within a range of 3-50 nm radius of curvature, attached on a flexible cantilever, interactions between the tip and material surfaces can be precisely detected. To further customize the equipment to our needs, the Nanonics MultiView 400™ system can be directly integrated into the Renishaw RM Series Raman Microscope together, as illustrated in Figure 2. These microscopes employ the upright microscope configuration, and the Nanonics MultiView 400™ is readily placed on the sample stage of such a microscope. The Nano-indentation/SPM system is a unique instrument for characterizing the elastic, plastic, stress-strain, hardness, creep, fracture, residual stresses and other mechanical properties of coatings, thin films, interface, bulk materials and the near surface region of materials. The microRaman system is capable of measuring spectra from both solid and liquid samples. Using this system, it is possible to investigate crystal structure, orientation, composition and stress. It is noted that all other systems we have investigated combining AFM and Raman perform an AFM scan or a Raman scan separately. The custom-designed system we purchased is the Nanonics-Renishaw combination, which provides simultaneous and on-line data from both modalities. This enormous advantage resolves critical problems in Raman such as intensity comparisons in Raman images and provides for new avenues of improved resolution and unique characterization. The Nanonics patented cantilevered optical fibers are held between the microscope lens and the sample without obstructing any aspect of the far-field optics. The tip in these fibers is exposed and illuminated by the lens of the microscope, allowing the user to view the exact region where the SPM and Raman information is being collected. With the combined system, one can now record, in parallel with Raman, a wide variety of scanned probe imaging modalities. For example, in MEMS, while the silicon (Si) Raman peak of a microcircuit is being monitored to detect stress in the silicon, the Raman spectroscopist can simultaneously measure the circuit's micro-topography with AFM, and its NSOM reflectivity or its electrical properties, such as the dopant concentration. In addition, Nanonics provides software that can display all these images at once for direct and simultaneous comparison and analysis



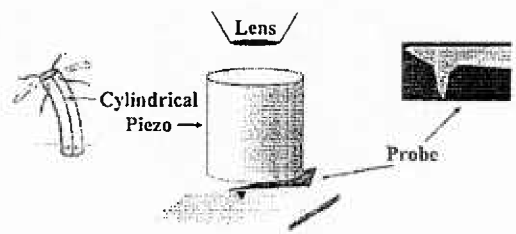


Figure 2. Schematic of the DURIP system. (Nanonics)

2.Current Status.

The actual experimentation on and testing of the Nanonics unit started right after the installation and training which took place in February 2009. The initial installation and training lasted a week and was then followed by a couple of online training sessions supported by the Nanonics company. These online training sessions are still ongoing from time by time, whenever the need arises.

Given the fact that the Nanonics Multiview 400 is composed of three different characterization techniques namely: scanning probe microscopy (SPM, or atomic force microscopy (AFM)), Nanoindentation and Raman Spectroscopy. In addition, besides having the capability of running individual scans for each technique, there is also the capability to run combined integrated experiments (AFM-Raman) and Nanoindentation-Raman. The following report briefly explains the experimentation procedure along with our recently obtained results so far from the unit in each of the categories:

2.1- Scanning Probe Microscopy (SPM) experiments

In running an SPM experiment, the first step is mounting the Nanonic SPM tip on the tip mount, using a pair of tweezers. Afterwards the tip mount is placed on the Nanonic head (Figure 3).

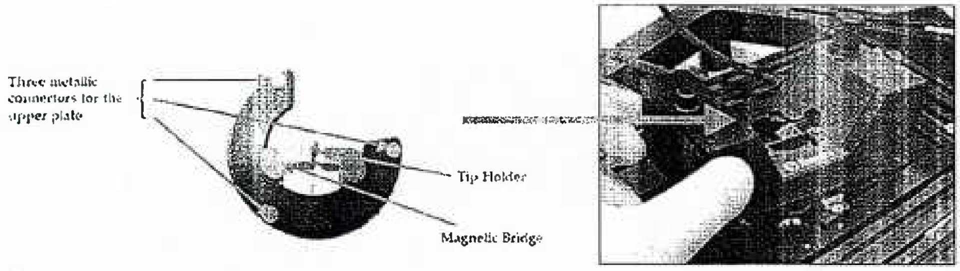


Figure 3. (a) AFM optical fiber probe tip (b) Nanonic head contained of two planes. The upper plane is where the tip mount is placed. The lower plane is used to mount the specimen.

The Nanonics Multiview 400 unit benefits from a Laser deflection beam feedback enabling an accurate control and online acquisition of tip's relative position based on Nanonics' head coordinate system. The process involves focusing the Laser beam onto a special place of the probe tip, by aims of a small mirror, and reflecting it onto the Position Sensitive Detector (PSD) as shown in Figure 4. Since, at the time of AFM experiment, the force applied by the interaction of the probe with the sample causes the probe to bend, the laser beam is deflected from its original position which will be detected by the PSD monitor.

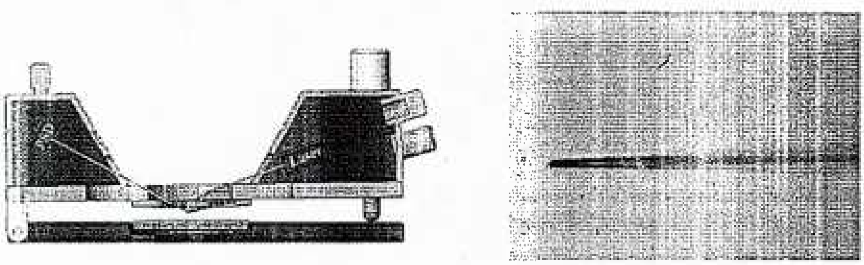


Figure 4. (a) a side view diagram of feedback laser and PSD monitor (b) An image of the right position of the laser on the probe tip.

Nanonics Multiview 400 enables us to run AFM scans in two different modes: 1- Contact mode, and 2- Intermittent or Tapping mode. In Contact mode, the tip is brought into contact with the sample followed by scanning a user-defined portion of the samples' surface in any desired direction. In the Intermittent mode, the probe tip would be oscillating in its resonant frequency and therefore the AFM scan is performed by a specific number of tapping motions of the tip per second on the surface. The contact mode is simpler and more user-friendly but since the tip is in complete contact with the sample at all times, it may cause some damage to the sample or to the tip. On the other hand, in the intermittent mode, since the tip is not in contact through most of its tapping cycle, the surface damage is less likely and also longer durability of the tip is expected. Figure 5 shows one of our desktop view while an AFM experiment is running. On the left side of the picture a live video of the scanning area is shown. On the right side, there is a height versus distance diagram (in blue) besides the error signal (in red) helping us to get the best AFM image by controlling the noise and error signal.

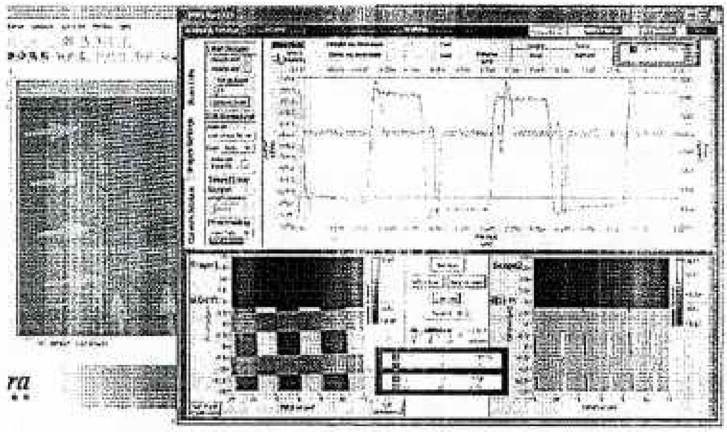
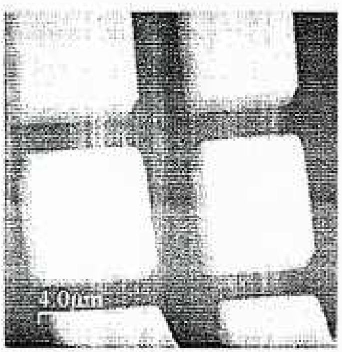


Figure 5. A desktop view of an ongoing AFM experiment

Figure 6-(a) shows an AFM image of a piece of Si-SiO_2 grid. White areas are lithographed silicone dioxide squares on a silicone substance. Figure 6-(b) shows our AFM experiment on a piece of Polyurethane (PUR) sample. As it could be seen in the picture, AFM allowed us to figure out the orientation of the crystalline regions versus amorphous ones in the PUR sample.



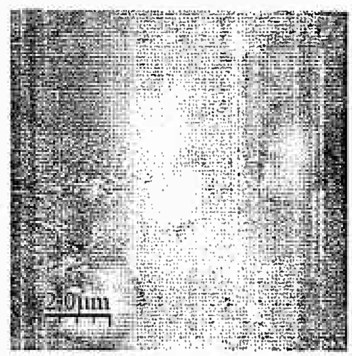


Figure 6. AFM image of (a) a Silicone chip (b) Polyurethane

2.2- Nanoindentation experiments

The mechanism of the nanoindentation in Nanonics Mutiview 400 is quite similar to the AFM experiments. The same Laser feedback system would be used for data acquisition but instead of AFM probe tip, nanoindentation tips are used. Nanoindentation is performed only in intermittent mode. After doing preliminary steps including focusing laser beam, adjusting PSD monitor and setting the resonant frequency of the tip, the calibration height-force graph should be generated. A sapphire glass with known properties is used for this purpose. The tip would land on sapphire glass and, since mechanical properties of the tip are known (such as its spring constant), the force of the tip would be calibrated for the actual experiment. Finally the nanoindentation would be run by replacing the sapphire glass with the sample in question. Figure 7 shows the force-height diagram loop after nanoindentation of a polyimide sample. Subsequently the unit provides us with the opportunity to capture an AFM image of the nanoindented area. Figure 8-(a) shows an AFM image of a nanoindented area using a diamond nanoindentation tip.

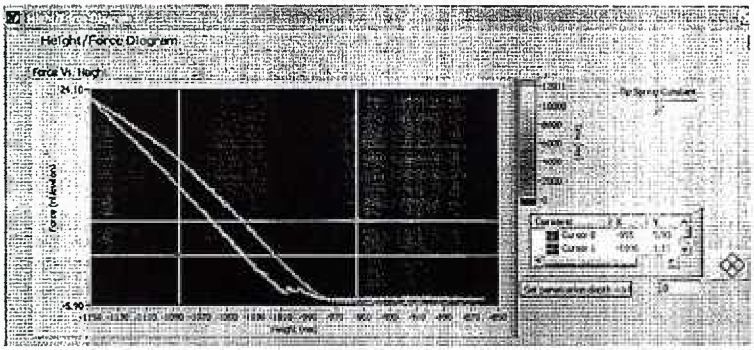


Figure 7. Force Height diagram of Polyimide sample

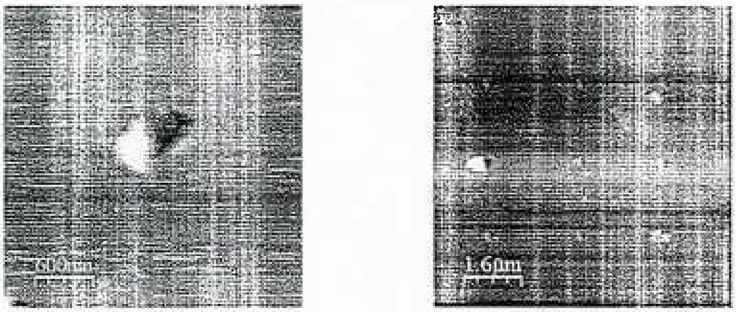


Figure 8 (a) Nanoindentation using a diamond tip (b) An array of Nanoindented points

The unit also allows for multiple consecutive nanoindentation experiment in which an array of points could be indented and desired mechanical properties could be measured by taking an average of them. Figure 8-(b) shows an AFM image of an array of Nanoindented points after running a multiple Nanoindentation test. The raw data of this Nanoindentation test is shown in Figure 9.

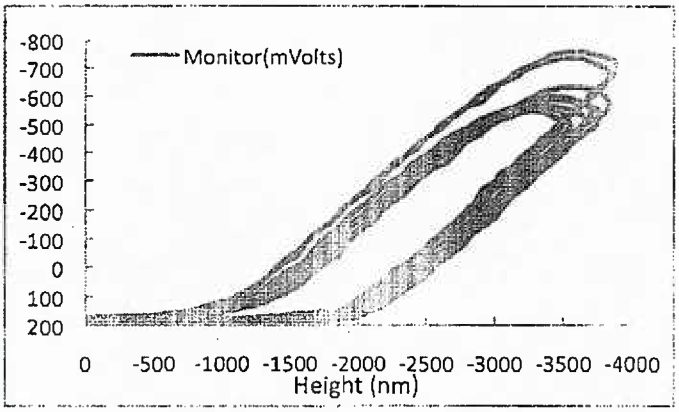


Figure 9. Multiple Nanoindented loops of an array of nanoindented points

It is worth noting that the nanoindentation tool could be used to scratch samples if writing or marking on the surface of the sample is desired.

2.3- Raman Spectroscopy

Nanonics Multiview 400 is equipped with a green Laser with 532nm wavelength for Raman spectroscopy measurements. The unit includes an optical fiber connection between the laser source and the optical microscope to direct the laser beam onto the Nanonics head. A 50x objective is used to bring a good focus of the beam on the sample. The reflected laser beam from the sample would be transferred to the Raman spectrometer, using another optical fiber, used for analyzing the resulting Raman Spectra. Figure 10 shows the Raman spectra of a silicone sample. The stoke peak of the silicone could be seen at a wavelength of around 547nm while a small anti-stoke peak is right on the other side of the laser peak but with weaker intensity.

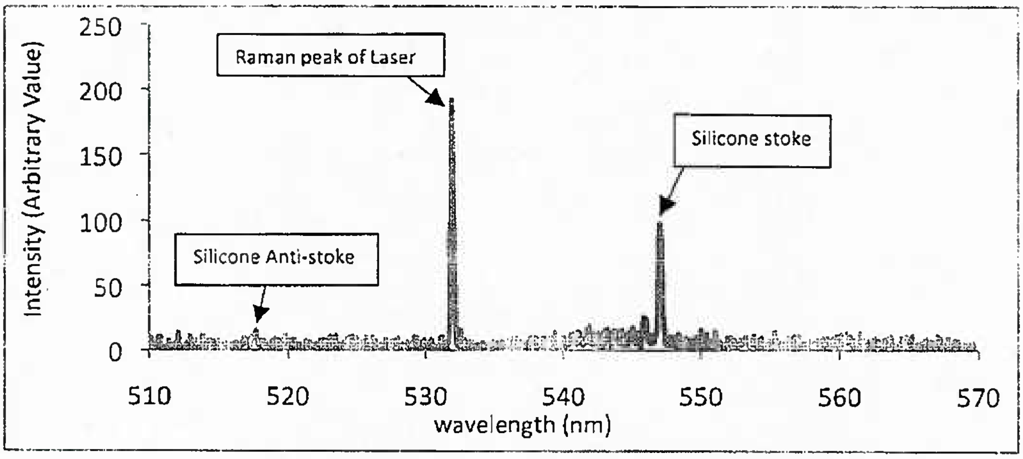


Figure 10. Raman Spectroscopy of a silicone sample

3. Future Focus on the Special Features

The unit is also capable of running combined microRaman/AFM experiments which gives a superior correlation of surface topography of a sample with its Raman spectra. Raman Spectroscopy software is also equipped with a visual contrast feature giving the operator the opportunity to superimpose the RAMAN image onto the topographic AFM image. Figure 11 shows a 3D collage image of this feature, which we have attempted. Mastering of this unique capability is ongoing, with continued support from Nanonics engineers. Our goal is to use this capability to further inform our research in active nanocomposites. The coupling of the SPM, nanoindentation and micro Raman will enable fundamental studies into; 1) investigating interfacial phenomena that include adhesion and phase transformation, 2) quantifying extremely localized and interfacial stress, 3) measuring the force magnitudes of the energetic electrons on particle surfaces when interacting to form different types of bonding, and 4) investigating particle interactions which is the most important and fundamental question in the understanding nanocomposite interfaces and mechanics. The understanding listed here will assist in our ongoing development of advanced materials, such as nanocomposites and active materials.

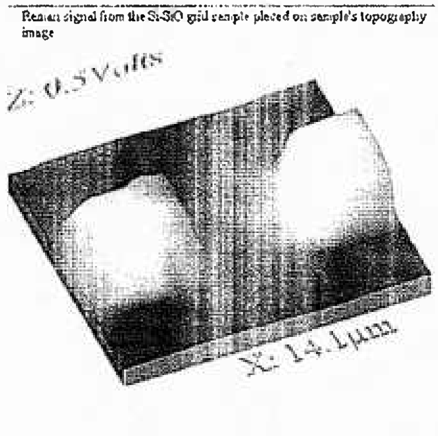


Figure 11. MicroRaman/AFM collage of Si-SiO_2 grid sample